

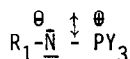
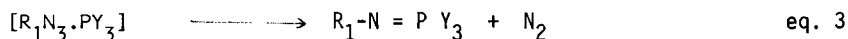
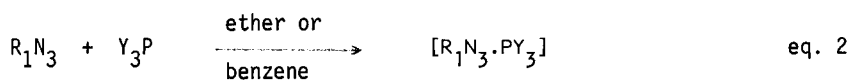
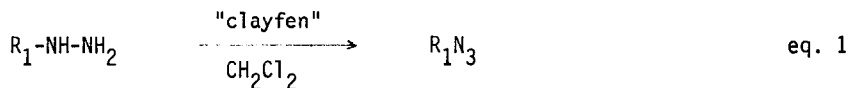
## FACILE CONVERSION OF HYDRAZINES TO IMINOPHOSPHORANES

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**Abstract** : Condensation of triphenylphosphine, triphenyl- and triethylphosphite with azides, easily available from our novel preparation, leads to iminophosphoranes.

We have earlier reported<sup>1</sup> a new preparation of azides in good yields under mild conditions using the extremely inexpensive clay-supported ferric nitrate ("clayfen"<sup>2</sup>). As a *coda* to this work, we now describe how it can easily be adapted to the preparation of iminophosphoranes, compounds widely used since the pioneering studies of Staudinger<sup>3</sup> for the synthesis of amines<sup>3-5</sup>, amides<sup>5</sup>, enamines and imines<sup>6</sup>, and of a variety of compounds with carbon-nitrogen double bonds<sup>3,7-11</sup>. Their utility is comparable to that of the Wittig reagents, to which they bear formal resemblance.

The classical synthesis of iminophosphoranes by the Horner procedure<sup>12</sup> is rather tedious. Because condensation of triphenylphosphine, triphenyl- and triethylphosphite with azides provides more direct access<sup>13</sup>, we have elected to follow the route outlined below :



where Y is C<sub>6</sub>H<sub>5</sub> (1a-d), C<sub>6</sub>H<sub>5</sub>O (2a-b) and C<sub>2</sub>H<sub>5</sub>O (3a-b). It is possible in favorable cases to isolate the intermediate complex formed (eq. 2), although in most instances it decomposes to the iminophosphorane at room temperature or below (Table). The experimental procedure is slightly different if the phosphine-azide pair is isolated, as in the case of 1a and 1b<sup>17</sup>. Otherwise, this is a one-pot reaction<sup>18</sup>. The purity of the isolated compounds is checked by determination of the consentaneous m.p., ir<sup>19</sup>, <sup>1</sup>H and <sup>31</sup>P nmr<sup>20</sup>, and tlc<sup>21</sup>.

Table : Iminophosphoranes Produced by Condensation of Azides with Triphenylphosphine, Triphenyl- and Triethylphosphite.

<u>R<sub>1</sub></u>	<u>Compound no.</u>	<u>m.p., °C</u>	<u>Isolated Yield (overall <sup>a</sup>, %)</u>
C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub>	<u>1a</u>	157-159 (lit. 158-159 <sup>14</sup> )	52
	<u>2a</u>	84-86 (lit. 85-86 <sup>15</sup> )	51
	<u>3a</u>	oil <sup>16</sup>	67
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	<u>1b</u>	186-188	50
	<u>2b</u>	62-64	52
	<u>3b</u>	oil <sup>16</sup>	64
C <sub>6</sub> H <sub>5</sub> CO	<u>1c</u>	191-193 (lit. 193-194 <sup>3</sup> )	47-50
C <sub>6</sub> H <sub>5</sub>	<u>1d</u>	129-131 (lit. 130-131 <sup>3</sup> )	46-48

<sup>a</sup> starting from the hydrazine.

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16. The crude oil is chromatographed on an alumina column using dichloromethane as eluent yielding the pure iminophosphorane.
17. Preparation of 1a and 1b : an equimolar amount of azide<sup>1</sup>, dissolved in ether (20 ml), is added dropwise to a stirred solution of triphenylphosphine (20 mmol) in ether (30 ml) at room temperature. There is no gas evolution. After leaving the reaction mixture stand for 15 min., the solids are filtered. The crude solids are added portionwise to hot benzene (40 ml), with vigorous gas evolution. The solution is then heated and stirred for 1h. After cooling, the white solid which has formed is collected, washed with benzene and dried under vacuum.
18. Preparation of 1c, 1d, 2a-b, 3a-b : the azide<sup>1</sup> (20 mmol) is dissolved in 30 ml of ether, and the solution is added to an equimolar solution of the corresponding triphenylphosphine or triphenyl- or triethylphosphite in the same solvent (20 ml) at room temperature. There is a strong evolution of gas. After 1h at room temperature (1c-d) or 2-3h at reflux (2a-b, 3a-b) the solids (crystallization of the product is induced by scratching the inside of the vessel) are filtered, washed and dried.
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  - (1a) ir (nujol mull,  $\text{cm}^{-1}$ ) :  $\nu_{\text{Ar-H}}$  = 3050 (w),  $\nu_{\text{Ar}}$  = 1580 (m),  $\nu_{\text{P-Ar}}$  = 1430, 1100, 1020, 990 (w-m),  $\nu_{\text{P=N}}$  = 1370(s),  $\nu_{\text{SO}_2}$  = 1260(s), 1130(s).
  - (1b) ir (nujol mull,  $\text{cm}^{-1}$ ) :  $\nu_{\text{Ar-H}}$  = 3050 (w),  $\nu_{\text{Ar}}$  = 1580 (m),  $\nu_{\text{P-Ar}}$  = 1430, 1100, 1020, 990 (m-w),  $\nu_{\text{P=N}}$  = 1370(s),  $\nu_{\text{SO}_2}$  = 1260(s), 1140(s).
  - (1c) ir (nujol mull,  $\text{cm}^{-1}$ ) :  $\nu_{\text{Ar-H}}$  = 3040 (w),  $\nu_{\text{Ar}}$  = 1580 (m),  $\nu_{\text{P-Ar}}$  = 1430, 1150, 1100 (m),  $\nu_{\text{C=O}}$  = 1540(s),  $\nu_{\text{P=N}}$  = 1320(s).
  - (1d) ir (nujol mull,  $\text{cm}^{-1}$ ) :  $\nu_{\text{Ar-H}}$  = 3050 (w),  $\nu_{\text{Ar}}$  = 1580 (m),  $\nu_{\text{P-Ar}}$  = 1430, 1100 (m),  $\nu_{\text{P=N}}$  = 1330(s).
  - (2a) ir (nujol mull,  $\text{cm}^{-1}$ ) :  $\nu_{\text{Ar-H}}$  = 3060 (w),  $\nu_{\text{Ar}}$  = 1580 (s),  $\nu_{\text{P=N}}$  = 1375 (m),  $\nu_{\text{SO}_2}$  = 1270(s), 1140-1170 (s),  $\nu_{\text{P-O-Ar}}$  = 1440(s), 1010(s), 960(s), 750(s).
  - (2b) ir (nujol mull,  $\text{cm}^{-1}$ ) :  $\nu_{\text{Ar-H}}$  = 3040, 3060 (w),  $\nu_{\text{Ar}}$  = 1580 (s),  $\nu_{\text{P=N}}$  = 1380 (m),  $\nu_{\text{SO}_2}$  = 1280(s), 1160 (s),  $\nu_{\text{P-O-Ar}}$  = 1450(s), 960(s), 810(s), 750(s).
  - (3a) ir (neat,  $\text{cm}^{-1}$ ) :  $\nu_{\text{Ar-H}}$  = 3060 (w),  $\nu_{\text{P=N}}$  = 1390 (m),  $\nu_{\text{SO}_2}$  = 1275(s), 1200 (s),  $\nu_{\text{P-O-C}_2\text{H}_5}$  = 1150(s), 1000-1080(s), 810(s).
  - (3b) ir (neat,  $\text{cm}^{-1}$ ) :  $\nu_{\text{Ar-H}}$  = 3050 (w),  $\nu_{\text{Ar}}$  = 1590 (m),  $\nu_{\text{P=N}}$  = 1390 (m),  $\nu_{\text{SO}_2}$  = 1260(s), 1200(s),  $\nu_{\text{P-O-C}_2\text{H}_5}$  = 1150(s), 1000-1100(s), 810(s).
20. The <sup>1</sup>H and <sup>31</sup>P nmr spectra are recorded on a Bruker AM 300 WB spectrometer operating in the Fourier transform mode at 300.13 and 121.49 MHz, respectively. Proton chemical

shifts are referenced to internal TMS and phosphorus chemical shifts are referenced to external  $\text{Ph}_3\text{P}$  ( $\text{CDCl}_3$ ) with downfield shifts taken as positive ( $\text{Ph}_3\text{P}$  chemical shift is taken equal 118 ppm in respect to 85%  $\text{H}_3\text{PO}_4$ ; see A.J. Gordon and R.A. Ford, The Chemist's Companion, Wiley, New York, 1972). NMR spectra :

- (1a)  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  7.18 (t, 1H,  $J=8\text{Hz}$ ), 7.38-7.47 (m, 9H), 7.55 (t, 2H,  $J=8\text{Hz}$ ), 7.62 (d, 2H,  $J=8\text{Hz}$ ), 7.68-7.77 (m, 6H);  $^{31}\text{P}$  ( $\text{CDCl}_3$ )  $\delta$  138.1 (s).
- (1b)  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  2.26 (s, 3H), 6.99 (d, 2H,  $J=8\text{Hz}$ ), 7.39-7.58 (m, 9H), 7.69-7.78 (m, 8H);  $^{31}\text{P}$  ( $\text{CDCl}_3$ )  $\delta$  137.7 (s).
- (1c)  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  7.34-7.56 (m, 12H), 7.97-7.87 (m, 6H), 8.35 (dd, 2H,  $J=1.7, 8.0\text{ Hz}$ );  $^{31}\text{P}$  ( $\text{CDCl}_3$ )  $\delta$  144.1 (s).
- (1d)  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  6.64 (t, 1H,  $J=8.0\text{ Hz}$ ), 6.80 (d, 2H,  $J=8.0\text{ Hz}$ ), 7.00 (t, 2H,  $J=8.0\text{ Hz}$ ), 7.38-7.52 (m, 9H), 7.71-7.79 (m, 6H);  $^{31}\text{P}$  ( $\text{CDCl}_3$ )  $\delta$  126.3 (s).
- (2a)  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  7.16-7.44 (m, 18H), 7.73 (d, 2H,  $J=8.0\text{ Hz}$ );  $^{31}\text{P}$  ( $\text{CDCl}_3$ )  $\delta$  101.7 (s).
- (2b)  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  2.33 (s, 3H), 7.09 (d, 2H,  $J=8.0\text{ Hz}$ ), 7.17-7.34 (m, 15H), 7.62 (d, 2H,  $J=8.0\text{ Hz}$ );  $^{31}\text{P}$  ( $\text{CDCl}_3$ )  $\delta$  101.5 (s).
- (3a)  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  1.31 (dt, 9H,  $J=1.2, 7.0\text{ Hz}$ ), 4.20 (dm, 6H,  $J=1.2, 7.0\text{ Hz}$ ), 7.40-7.49 (m, 3H), 7.93-7.98 (m, 2H);  $^{31}\text{P}$  ( $\text{CDCl}_3$ )  $\delta$  120.1 (m,  $J=8.3\text{ Hz}$ ).
- (3b)  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  1.32 (t, 9H,  $J=7.1\text{ Hz}$ ), 2.38 (s, 3H), 4.21 (m, 6H,  $J=7.1\text{ Hz}$ ), 7.23 (d, 2H,  $J=8.0\text{ Hz}$ ), 7.82 (d, 2H,  $J=8.0\text{ Hz}$ );  $^{31}\text{P}$  ( $\text{CDCl}_3$ )  $\delta$  120.1 (m,  $J=8.3\text{ Hz}$ ).

21. Thin layer chromatography is run on silica gel plates Polygram SilG/UV<sub>254</sub> and hexane/ethyl acetate (6:4) is used as solvent in all cases. Approximate  $R_f$  values for iminophosphoranes are 0.15-0.44. The developed spots are visualized by UV light.

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